

## Micropore effect on dissociation process of methane hydrate and fractionation of stable isotopes

OTA, Yuka<sup>1\*</sup> ; HACHIKUBO, Akihiro<sup>1</sup> ; TAKEYA, Satoshi<sup>2</sup>

<sup>1</sup>Kitami Institute of Technology, <sup>2</sup>National Institute of Advanced Industrial Science and Technology (AIST)

Gas hydrates are clathrate compounds that the guest-gas molecules are trapped in host-cages composed of water molecules, and are stable at low temperatures and high pressure conditions. Natural gas hydrate exists in the sea bottom sediments off Sakhalin Island (Sea of Okhotsk), those comprised of diatom with many small pores. Sediment particles may affect to formation and dissociation processes of gas hydrate because their small pores change equilibrium pressure of gas hydrate. Isotopic fractionation of guest gas between gas and hydrate phases has been reported (Hachikubo *et al.*, 2007), however, little is known about the effect of micropore on the fractionation of stable isotopes. We conducted calorimetric measurements of methane hydrates (MH) formed with silica-gel pores to investigate thermal properties of MH in the small pores, and measured isotopic difference in methane molecules between MH and residual gas at their formation process.

The silica-gel sample (pore diameter: 15 nm) was dried at 423 K for 24 hours and then adsorbed water in a chamber for three days. Methane hydrates were formed with the adsorbed water in silica-gel pores under high pressure of methane (10 MPa) at 273.2 K. Silica-gel samples with methane hydrate were stored in liquid nitrogen and the residual gas was also sampled. Thermographs of the hydrate sample were obtained by a calorimeter. Stable isotopes (carbon and hydrogen) of hydrate-bound and residual methane were measured by an IRMS.

The thermograph revealed that a broad peak around 173 K and other peaks ranged from 193 K to 203 K corresponded to dissociation of pore and bulk hydrates, respectively. Because the dissociation of hydrate formed ice and plugged the pores, a large endothermic peak appeared in the range from 223 K to 273 K and the internal pressure increased due to dissociation of confined hydrate.

$\delta D$  of hydrate-bound methane was 6.2-7.2 ‰ lower than that of residual methane in the formation processes, agreed fairly with the result of Hachikubo *et al.* (2007). While there was no difference in the case of  $\delta^{13}C$  (Hachikubo *et al.*, 2007), our results showed that  $\delta^{13}C$  of hydrate-bound methane was several ‰ higher than that of residual methane, suggesting effect of micropores.

Hachikubo A, Kosaka T, Kida M, Krylov A, Sakagami H, Minami H, Takahashi N, Shoji H (2007) Isotopic fractionation of methane and ethane hydrates between gas and hydrate phases. *Geophys Res Lett* **34**: L21502. doi:10.1029/2007GL030557

Keywords: gas hydrate, micropore, diatom, stable isotope, isotopic fractionation, calorimetry